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PROPERTIES STUDY OF ANHYDRITE(II) PREPARED FROM WASTE GYPSUMS

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Abstract

Anhydrites(II)-β $CaSO_4$ were prepared from two waste gypsums (PRECHEZA Přerov, FOSFA Poštorná). The samples of anhydrites(II) with sulphate activators were tested on spillage, beginning and the end of setting time, bending and pressure strength. Both sodium and potassium sulphates accelerated setting of anhydrite, more impressively that prepared from Poštorná gypsum. The addition of Na_2SO_4 influenced the strength of this anhydrite very favourably. On the contrary K_2SO_4 influenced favourably the strength of Přerov anhydrite. Results confirm the necessity to evaluate properties of such materials with respect to their origin.

Keywords: anhydrite(II), setting, strength, waste gypsum

Introduction

Development of industry in the last decades has led to an increase of gas emissions into the atmosphere. The requirement for a reduction in the sulphur oxides content of gas emissions has created a big amount of waste gypsum $-CaSO_4 \cdot 2H_2O$. Waste gypsum is also produced as a necessary by-product by several chemical manufacturers. The amounts created at the present time, and in the near future, when air pollution caused by sulphur oxides will be dealt with more rigorously, are estimated to be hundreds of thousands of tons a year in both the Slovak and Czech Republics. Storage of such an amount of solid material in free dumps threatens devastation to the landscape, agricultural land and water sources. Seeking possibilities for waste gypsum to be used as a raw material for further industrial manufacturing is unavoidable.

The results presented in this work were obtained in a research concerning the possibilities of preparation of slowly hardened plaster (anhydrite II) from the following waste gypsums:

1. PRECHEZA Přerov (titanium white production)
2. FOSFA Poštorná (phosphoric acid production)

The aim of this work was to evaluate the properties of anhydrite(II) prepared from the above waste gypsums.

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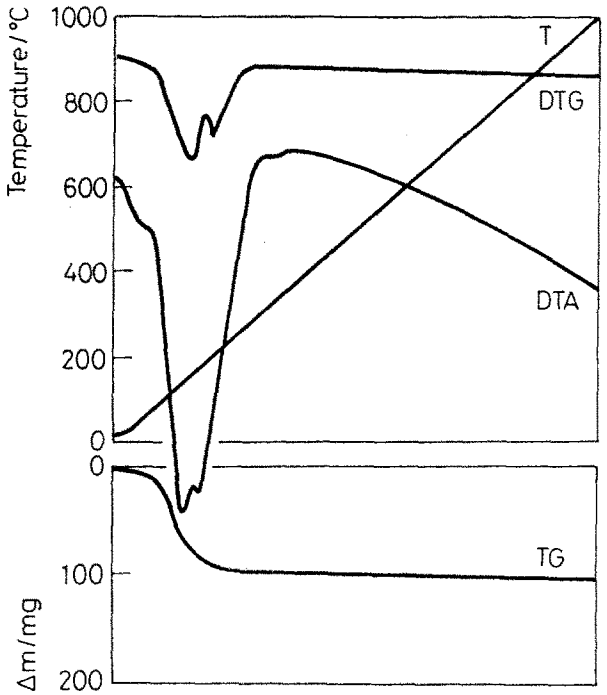

Fig. 1 DTA, TG and DTG curves of waste gypsum PRECHEZA Přerov

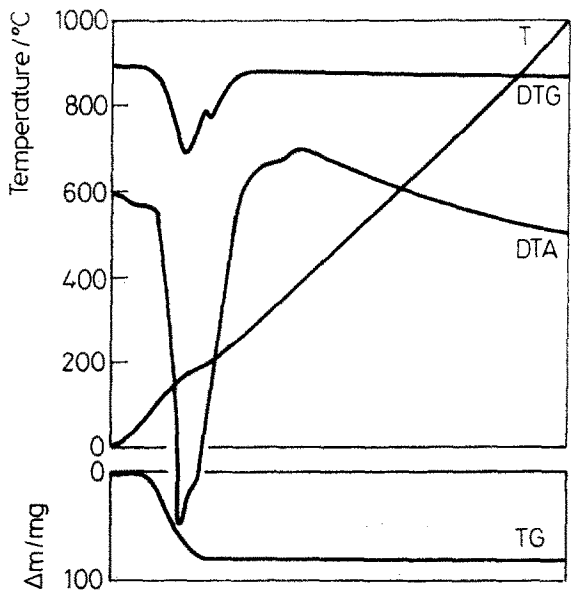

Fig. 2 DTA, TG and DTG curves of waste gypsum FOSFA Poštorná

Experimental

Anhydrite(II), that means beta-$CaSO_4$, is possible to prepare in the temperature range from 200 to 1080°C [1–3].

DTA results were used for the determination of the temperature range for waste gypsum treatment. DTA curves are shown in Figs 1 and 2.

The following temperature procedure was chosen for anhydrite(II) preparation:

- samples were inserted into a cold furnace
- temperature was increased to 850°C during 3.5 h
- temperature was held at 850°C during 4 h
- cooling was lowered up to 150°C during 4 h
- removing the samples.

The chemical composition of both used waste gypsum is shown in Table 1.

Table 1 Chemical composition of used gypsums

Component determined	Content of component in weight %	
	Poštorná	Přerov
humidity (50°C)	0.07	0.41
bound water	18.56	17.52
SiO_2	1.25	4.22
Al_2O_3	2.30	5.60
Fe_2O_3	0.28	8.90
CaO	34.43	26.89
MgO	0.00	2.26
SO_3	42.98	34.05
P_2O_5	0.00	0.08
sum	99.87	100.10
% of dihydrate	88.68	73.22
% of anhydrite	2.95	0.00

A muffle furnace was used to dehydrate the samples. Gypsum transformation to anhydrite(II) was evaluated on the basis of TA results. Conversion detection under the described conditions was shown to be 96% for Přerov gypsum and 97% for Poštorná gypsum, respectively.

Properties of prepared anhydrite(II)

To evaluate qualitative properties, the following examinations were carried out on the prepared anhydrite samples:

- spillage test according to ON 74 4592

– the beginning and the end of setting according to ČSN 72 2301
– strength tests in bending and pressure on modified prisms 2×2×8 cm.

Following sulphates were used as hydration activators: sodium, potassium and iron(II) in amounts of 2 and 3 weight % and their combinations: 1.5%$FeSO_4$ + 1%Na_2SO_4 and 1.5%$FeSO_4$ + 1%K_2SO_4.

The examination of mechanical strength on both prepared anhydrites were done after exposing the samples for 3, 7 and 15 days at ambient laboratory conditions (relative humidity of 80%, temperature of 20±2°C).

Results and discussion

Spillage

The aim of this test, in terms of the ON 74 4592 item 43, is to determine the water/solid ratio necessary to achieve a mixture spillage of 200–240 mm from the filled coniform Vicat apparatus vessel with a lower diameter of 75 mm, upper of 65 mm and a height of 40 mm.

This test is used to determine if anhydrite is suitable for a shed anhydrite paint.

The following values of water/solid ratio correspond to anhydrites prepared from waste gypsum:

Přerov anhydrite $w=0.83$

Poštorná anhydrite $w=0.39$.

The beginning and the end of setting

The progress in setting was observed for both the prepared anhydrites with the addition of 2 and 3 weight % of activators (Na_2SO_4 and K_2SO_4).

The results are shown in Table 2. It is necessary to note that the setting of both the prepared anhydrites(II) without an added activator did not occur at all for 24 h and therefore the corresponding results are not shown in the table.

Both ingredients used accelerate the progress of setting. In the investigated concentration region the setting time is shortened with the increase of the setting regulator content. The increase of an ingredient content over 3 weight % has no practical significance.

Having compared experimental results, it is obvious that the influence of setting activators is more significant on the anhydrite(II) samples prepared from Poštorná gypsum.

To compare the above-mentioned results, the beginning and the end of setting of the other anhydrite(II) is shown. This anhydrite was prepared under the same conditions as the previous one, but using a natural gypsum Koběřice (content of anhydrite was 0% and of dihydrate 69%) instead of a waste gypsum and

Table 2 Setting progress of anhydrite prepared from Přerov and Poštorná gypsums. The time corresponds to hours

Activator	Beginning of setting		End of setting	
addition/wt%	Přerov	Poštorná	Přerov	Poštorná
Na_2SO_4–2%	12	1.8	20–24	4
Na_2SO_4–3%	7–8	1.6	18–24	3.5
K_2SO_4–2%	6–7	3.5	20–24	6
K_2SO_4–3%	2–3	1.5	4	4

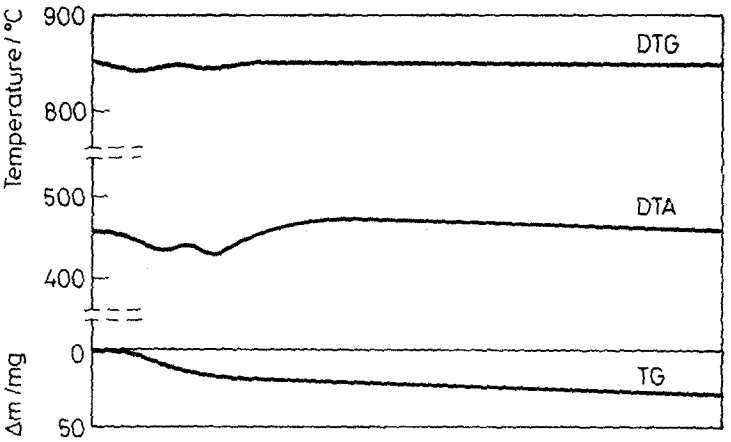

Fig. 3 DTA, TG and DTG curves of hydrated anhydrite prepared from natural gypsum, after 24 hours of hydration, respectively

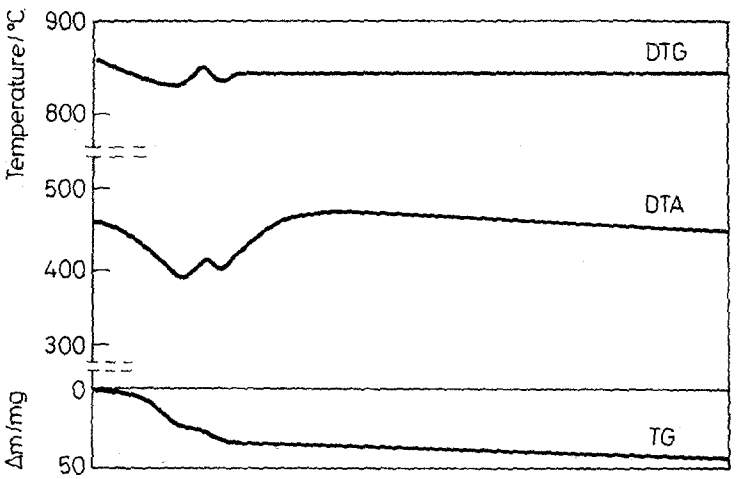

Fig. 4 DTA, TG and DTG curves of hydrated anhydrite prepared from natural gypsum, after 48 hours of hydration, respectively

the setting activator was added in an amount of 2% Na_2SO_4. The experimentally determined beginning of setting is 3 h 10 min. The setting of anhydrite ended after 4 h 50 min. The progress of setting was determined on samples prepared at a water/solid ratio 0.36.

The hydration course on samples of anhydrite(II) prepared from natural gypsum was observed using DTA. Samples prepared at a water/solid ratio of 0.5 without a setting activator were, after 24, 48 and 72 h of the hydration process, washed by acetone and the content of chemically bounded water was observed by DTA (temperature increase was 10°C min^{-1} till 1000°C). The results showed that after 24 h hydration the content of chemically bounded water is 2.2%, after 48 h twice so. After 72 h of hydration it increases to 12.5 weight %, which corresponds almost to a 60% conversion of anhydrite to gypsum. In all the mentioned cases the sample weight was the same (900 g). DTA records of these determinations are shown in Figs 3–5.

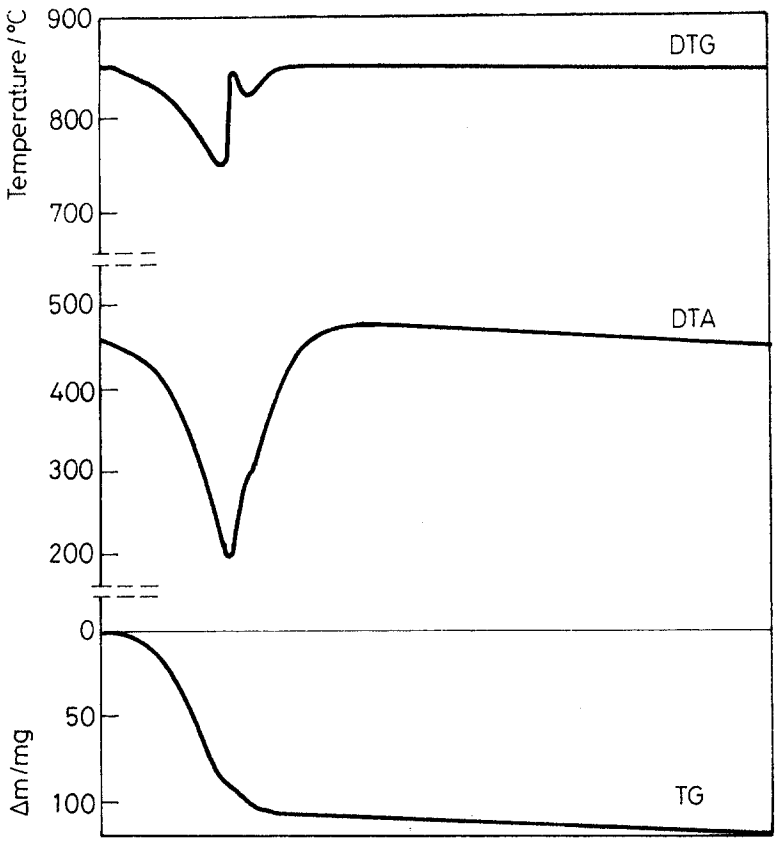

Fig. 5 DTA, TG and DTG curves of hydrated anhydrite prepared from natural gypsum, after 72 hours of hydration, respectively

Mechanical properties

The addition of setting regulators is also necessary to evaluate for their influence on mechanical properties.

The results of strength tests of samples exposed in laboratory conditions (r.h. 80%, $t=20\pm2°C$) are shown in Tables 3 and 4.

Table 3 Strength of prisms prepared from anhydrite Přerov after 3, 7 and 15 days

Activator addition/wt%	Strength in MPa					
	in bending			in pressure		
	3 days	7 days	15 days	3 days	7 days	15 days
Na_2SO_4–2%	2.25	3.28	3.89	7.75	8.33	7.40
Na_2SO_4–3%	2.55	3.63	3.62	8.20	10.38	8.51
K_2SO_4–2%	2.10	3.12	1.92	8.00	6.81	4.45
K_2SO_4–3%	2.40	4.27	3.96	9.20	11.63	7.82
$FeSO_4+K_2SO_4$	0.69	1.44	1.20	2.29	4.35	2.51
$FeSO_4+Na_2SO_4$	1.07	3.05	2.75	3.38	6.72	7.03

Table 4 Strength of prisms prepared from anhydrite Poštorná after 3, 7 and 15 days

Activator addition/wt%	Strength in MPa					
	in bending			in pressure		
	3 days	7 days	15 days	3 days	7 days	15 days
Na_2SO_4–2%	4.43	9.37	9.99	20.83	24.82	28.97
Na_2SO_4–3%	10.62	10.04	7.48	25.43	26.24	29.93
K_2SO_4–2%	1.02	1.71	1.41	3.57	2.69	3.25
K_2SO_4–3%	1.44	2.49	1.75	4.24	3.66	4.66
$FeSO_4+K_2SO_4$	1.40	1.31	1.34	3.34	3.46	3.43
$FeSO_4+Na_2SO_4$	2.67	2.63	2.63	9.61	7.94	8.40

The strength test results in bending and pressure after 3 days showed that the Na_2SO_4 influences very favourably the strength of Poštorná anhydrite, relatively less of Přerov anhydrite. On the contrary, the use of K_2SO_4 more favourably influences the strength of Přerov anhydrite, particularly in an amount of 3 weight%. K_2SO_4 with Poštorná anhydrite showed the least favourable influence from all of the activator combinations used.

According to the strength tests, after 7 days the increase of strength is comparable with that determined after 3 days. The addition of K_2SO_4 causes strength of Přerov anhydrite to be twice higher than Poštorná. The combination of $FeSO_4$ activator with alkali sulphates did not prove to be successful.

The results of strength tests after 15 days displayed some irregularities, whose causes are not known at this stage and which will be investigated in a further study.

The strength results obtained correspond to the influence of tested additives on the setting progress of both the examined anhydrites.

Conclusions

The results obtained show differences in properties of both the prepared anhydrites which confirm the necessity to evaluate the properties of binding materials prepared from gypsum according to its origin.

Our tests also confirmed the different efficiency of hydration activators used and simultaneously disclosed irregularities in the time development of mechanical properties.

The causes of different effects of ingredients used on tested anhydrites could be derived from the different chemical compositions of the initial waste gypsums. The problem will be investigated in the future. Its clarifying will enable us to assess the suitability of waste gypsums for different purposes in the production of building materials.

References

1 J. Hlaváč, Základy technologie silikátů, SNTL, Praha, 1981.
2 J. Bláha, H. Hanušová and J. Jedlička, Stavivo, 2 (1988) 51.
3 F. Škvára and J. Šobrová, Silikáty, 20 (1976) 149.